1,5-Pentanediol as an Oxygen Precursor for Atomic Layer Deposition of Zinc Oxide Thin Films

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S *Supporting Information*

Atomic layer deposition (ALD) is a vacuum deposition technique to grow a thin film via chemical adsorption.[1] Owing to its thickness controllability in atomic scale and conformal growth behavior through self-limiting chemisorption, the ALD method has been widely used in various applications such as electronic devices (e.g., memories and transistors), solar cells, and nanostructured materials.[2−4]

For a successful ALD of a thin film, suitable chemical precursors are required for each component element. Various types of ligands such as halides, alkyls, alkoxides, and amides have been studied to prepare metal precursors that have high volatility, thermal stability, and chemical reactivity on the surface.[2,5] Among the metal precursors, trimethylaluminum (TMA) and diethylzinc (DEZ) are well-known as excellent Al and Zn precursors, respectively. On the other hand, studies on the oxygen precursor are rare, because water or ozone can play a role of the oxygen precursor for ALD of metal oxides. Even though water and ozone satisfy the precursor requirements for ALD, sometimes it is not suitable to use water or ozone, especially on a labile substrate. For example, recently, Martinson et al. reported a nonhydrolytic ALD of Al_2O_3 from aluminum triisopropoxide and acetic acid on a light absorber of methylammonium lead halide for perovskite solar cells, because the perovskite layer is very sensitive to moisture even at room temperature.[6] Ritala et al. also proposed a nonhydrolytic ALD chemistry for metal oxide thin films in which a metal alkyl is used as a metal precursor and a metal alkoxide plays both roles of metal and oxygen sources.[7] By using the combination of trimethylaluminum and aluminum triisopropoxide, they obtained an abrupt interface between Al_2O_3 and Si substrate without an interfacial SiO_2 which can be formed by oxidation of the surface of Si substrate.

Here we report the use of 1,5-pentanediol (PD) as an organic oxygen precursor. For ALD of metal oxides, the organic oxygen precursor must react with a metal precursor chemisorbed on the surface, leaving oxygen atoms (e.g., hydroxyl group), and the other organic moiety should be removed as a gaseous byproduct. To accomplish both the formation of hydroxyl group and the removal of the organic moiety, we chose PD as an oxygen precursor molecule.

There are several reports on the use of diols in ALD in order to prepare organic–inorganic hybrid polymer films that are called metalcones.[8−10] For example, the sequential exposure of TMA and ethylene glycol (1,2-ethanediol) in ALD process enables to grow an alucone thin film of poly(aluminum ethylene glycol) polymer which contains the moiety of ethylene glycol in the film.[8] Similarly, a zincone thin film can be prepared by ALD from DEZ and ethylene glycol.[9] Although PD also belongs to the family of diols, its surface reactions with alkylmetals may be essentially different from those of other diols.

Scheme 1 shows a proposed reaction pathway for the ALD of ZnO from DEZ and PD. The first half-reaction (denoted with "A" in Scheme 1) is identical to that of the typical ZnO ALD using DEZ and H_2O.[11] The adsorption sites (mainly, hydroxyl group) are occupied by DEZ, and the surface is terminated by ethylzinc species, liberating ethane as a byproduct. In the second half-reaction (B), the PD molecules react with the ethylzinc to form hydroxylzinc species on the surface, and both ethane and tetrahydropyran (THP, $C_5H_{10}O$) may be liberated as gaseous byproducts. As a result, the exposure of PD may give rise to recover the hydroxyl sites on the surface for the subsequent DEZ exposure. It should be noted that the organic moiety of PD can cleanly be removed by forming THP in the second half-reaction. This is the reason that we chose PD as an oxygen precursor molecule. According to the proposed pathway, the overall reaction between DEZ and PD is highly exothermic with a standard enthalpy of reaction ($\Delta_r H°$) of −358.7 kJ/mol, which is comparable to that (−335.1 kJ/mol) of the overall reaction between DEZ and H_2O (see the Supporting Information).
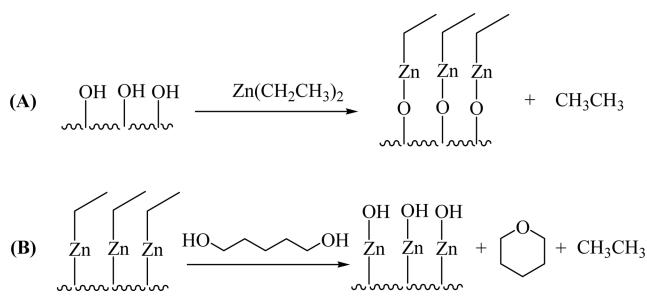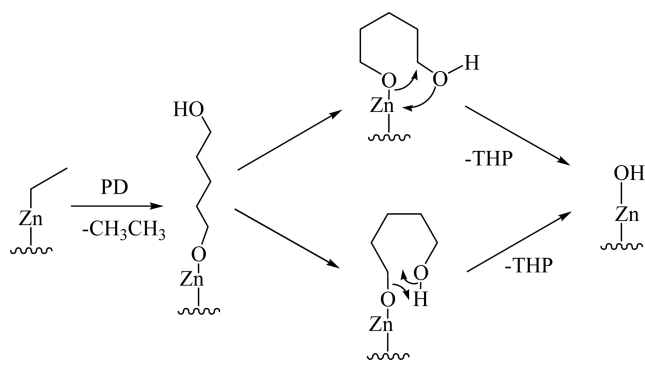
As shown in Scheme 2, an intermediate of 1-hydroxylpentanyl group will be formed on the surface during the second half-reaction (B). Subsequently, the intermediate may experience an intramolecular cyclization reaction to leave the hydroxyl group and to from the byproduct of THP. Recently, it was also reported that the conversion of PD into THP via intramolecular cyclization can be catalyzed on zeolites.[12,13]

To confirm the self-limiting growth of ZnO using PD as an oxygen precursor, we monitored variation of ZnO thickness depending on the exposure times of DEZ (x) and PD (y). The ALD experiments were performed with a long purge time (20 or 30 s) of PD in order to achieve complete removal of excess PD (see Figure S1). Figure 1a shows the self-limiting adsorption of DEZ on the OH sites in the first half-reaction. As the exposure time (x) of DEZ increases, the ZnO thicknesses grown for 100 ALD cycles saturate in both PD and water processes. However, the thickness by the typical ALD process using DEZ and water is significantly thicker than that by our new ALD process using DEZ and PD. It reveals that

Scheme 1. Plausible Reaction Pathway for ALD of ZnO from DEZ and PD

Scheme 2. Plausible Mechanisms for the Second Half-Reaction of ZnO ALD from DEZ and PD

Figure 1. ZnO thicknesses as functions of (a) DEZ exposure time (x) and (b) PD exposure time (y). ALD was performed at 80 °C for 100 cycles. The sequence times (in second) of DEZ exposure-purge-PD exposure-purge were x-10-4-20 in Figure 1a and 30-10-y-30 in Figure 1b. The error bar denotes the standard deviation of ZnO thickness in 6-in. wafer.

the adsorption sites of hydroxyl group are less abundant in the new process, because of the bulkiness of the intermediate (i.e., 1-hydroxylpentanyl) forming the hydroxyl sites and the formation of THP. The THP molecules may weakly adsorb on the ethylzinc-terminated sites which is not yet reacted. It is well-known that various ether compounds can coordinate metal ion as a neutral ligand. However, due to the weak coordination, THP will be liberated in the subsequent purging step. As a result, the adsorption site is less abundant comparing to the DEZ/water process. In Figure 1b, the adsorption of PD on the ethylzinc sites is also self-limiting in the second half-reaction, as indicated by the saturation of the ZnO thickness at long exposure time (y > 3 s) of PD.

In Figure 2, growth-per-cycle (GPC) of ZnO ALD using DEZ and PD is shown as a function of growth temperature. Each GPC was determined by taking a slope in the plot of ZnO thickness versus number of ALD cycles at a particular temperature (see Figure S2a). Below the growth temperatures of 100 °C, the GPC increases with temperature, because the adsorption reactions between precursors and adsorption sites are more reactive at higher temperatures. It should be noted that GPC of the typical ALD using DEZ and H₂O dramatically varies with the growth temperatures.[14,15] Especially, it rapidly decreases with temperature (above 150 °C) in the typical ZnO ALD, since the number of OH sites may decrease at higher temperature by dehydroxylation, forming bridged oxygen atoms. However, for the ZnO ALD using DEZ and PD, there is no significant variation of the GPC in a temperature range of 100−250 °C (see Figure S2b). It can be explained by the formation of gaseous THP molecules in the second-half reaction. Comparing to the second half reaction of the typical ALD in which only ethane molecules are liberated, both ethane and TPH molecules are generated as gaseous byproducts in the second half-reaction using PD. As a result, the formation of OH
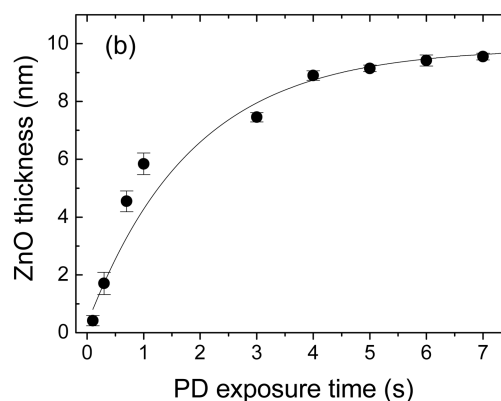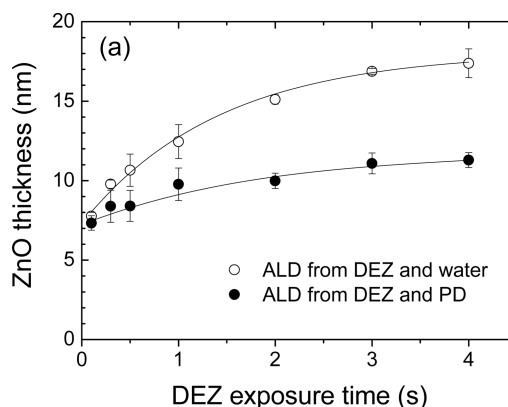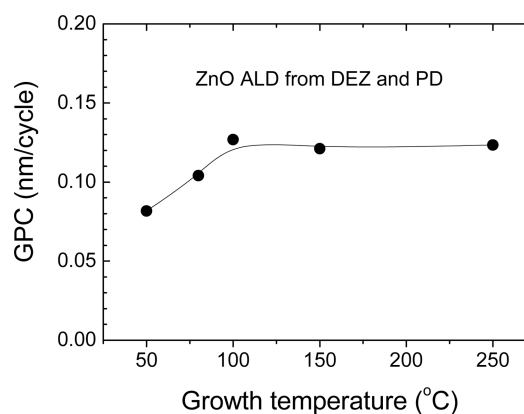

Figure 2. Temperature dependence of growth-per-cycle (GPC) in ZnO ALD using DEZ and PD. DEZ-Purge-PD-purge = 3-10-4-20 in second.

sites is more favored at higher temperature by the entropy effect in our ALD process.

In Figure 3, the composition of the ZnO film grown at 80 °C from DEZ and PD was analyzed by profiling the atomic concentrations of zinc, oxygen and carbon atoms in the direction of the film depth by X-ray photoelectron spectroscopy (XPS). The concentration ratio (~0.98) of oxygen to zinc is very close to the theoretical stoichiometric ratio (O/Zn = 1) of
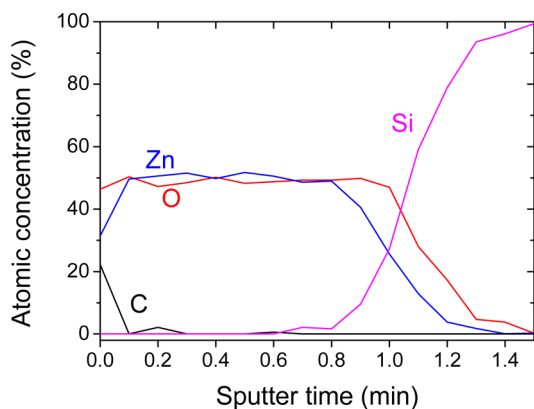
Figure 3. XPS depth profile of ZnO thin film grown at 80 °C by ALD using DEZ and PD.
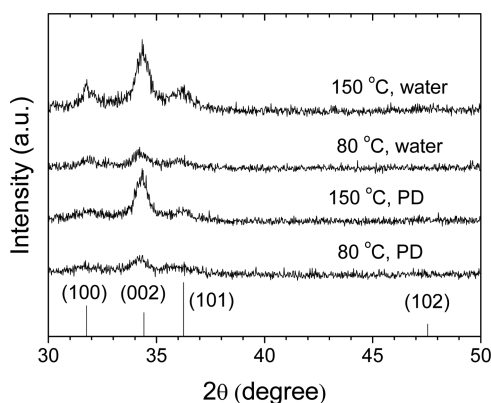

Figure 4. X-ray diffractograms of ZnO thin films grown at 80 or 150 °C by ALD using DEZ/PD or DEZ/H$_2$O. The characteristic peaks of the wurtzite structure of ZnO are drawn together for comparison.

Figure 5. HR-TEM images of ZnO thin films grown on Si at 150 °C by ALD using the processes of DEZ/H$_2$O (a) and DEZ/PD (b). The exposure times (y) of H$_2$O and PD in each process was 1 and 4 s, respectively. Prior to each ALD process, the native SiO$_2$ on Si substrate was removed by using a dilute aqueous HF solution.

ZnO. Furthermore, the carbon atoms are nearly not detected except the adventitious carbon on the surface, even though the PD is an organic oxygen precursor. In comparison, the ZnO film grown at the same temperature by the typical ALD process using DEZ and water is less stoichiometric with the ratio of O/Zn ~ 0.79, as shown in Figure S3. It is well-known that the ZnO films grown by ALD using DEZ and water have various defects such as zinc interstitial and oxygen vacancy that result in the *n*-type conductivity. The lower value of O/Zn than the stoichiometric ratio is due to the presence of the defects. However, because the new process of DEZ/PD exhibits slower GPC than the DEZ/water process, the formation of the defects will be less severe. Indeed, in the current density−voltage (*J*−*V*) curves (Figure S4) of the *n*-ZnO/*p*-Si diodes fabricated by the two processes, the diode made by the DEZ/PD process shows lower forward current density than one made by the DEZ/water process, because the former may have lower electron concentration than the latter.

The crystallinity of 10 nm-thick ZnO films was compared at two growth temperatures of 80 and 150 °C in both ALD processes (Figure 4). All of the ZnO films exhibit characteristic peaks of the hexagonal wurtzite structure, regardless of the oxygen precursor and the growth temperature, although the peaks are weak due to their thin thickness (~10 nm). It is well-known that the orientation of ALD-ZnO films dramatically varies with deposition temperature. According to the previous reports,[16,17] the (002) reflection is dominant at the deposition temperatures below 70 °C, indicating that ZnO grows with the
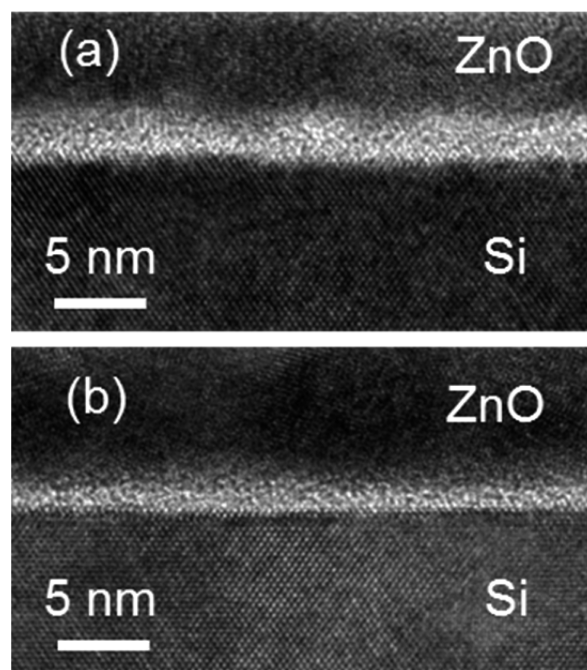
c-axis perpendicular to the substrate. However, above 70 °C, the (100) reflection becomes more and more prominent until at around 160−200 °C, revealing that the *a*-axis of ZnO is perpendicular to the substrate. Our ALD temperatures of 80 and 150 °C are included in the temperature range in which the (002) reflection appears with the (100) peak. The XRD patterns (Figure 4) of ZnO films are similar to those of the previous reports.[14,16−18] Note that there is no significant difference in XRD patterns between the ZnO films that are grown by the typical ALD process and the new ALD processes, if they are deposited at the same temperature. In addition, the surface roughness of ZnO films grown at 80 °C, of which thicknesses are around 10 nm, is investigated by atomic force microscopy (AFM) in Figure S5. The root-mean-square (RMS) roughness of the ZnO films grown by the DEZ/water and DEZ/PD processes are 10 and 3.9 Å, respectively. These are similar to the RMS values of the previous reports in which the RMS roughness varies between 4−40 Å at low growth temperatures.[19,20]

We investigated the interface between ZnO and Si substrate by using high resolution transmission electron microscopy (HR-TEM), in order to identify the extent of oxidation of the Si substrate during ALD process. Because Si has a high affinity toward oxygen and the Si substrate are directly exposed to an oxygen precursor for initial few cycles, an interfacial layer of SiO$_2$ is easily formed via the oxidation of the silicon surface in the initial stage of the ALD process.[7] However, in our ALD chemistry, we use PD as a mild oxidant instead of using water, which is a stronger oxidant than PD. Therefore, it is expected that the extent of oxidation of the Si surface may be significantly different between the typical ALD using water and our new chemistry using PD. Indeed, the thickness of the interfacial oxide (bright layer in Figure 5b) by the new ALD process is only half the thickness of the interfacial oxide by the

conventional process, even though the exposure time of PD is four times longer than that of water.

Finally, it is expected that TMA also exhibits the similar chemistry to form Al_2O_3 by using PD as an oxygen precursor. Indeed, the film grown from TMA and PD has been characterized to be Al_2O_3 by XPS analysis (Figure S6). Furthermore, according to our unpublished work,[21] ZnS thin film can also be grown by ALD using DEZ and 1,5-pentanedithiol which is the sulfur analogue of PD.

In summary, we propose a novel ALD route toward ZnO thin films in which PD is used as an organic oxygen precursor. Even though PD has an organic moiety in the chemical structure, the exposure of PD in the sequence of DEZ-purge-PD-purge results in the incorporation of oxygen without carbon residue. Since PD is a mild oxidant comparing to water or ozone, this process will be useful for ALD on labile substrates.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.6b05300.

> Experimental details, ZnO growth behavior as a function of a PD exposure time, number of cycles, and growth temperature, XPS depth profiles, $J-V$ curves of n-ZnO/p-Si diodes, AFM images, and thermodynamic data table (PDF)

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Notes

The authors declare no competing financial interest.

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1,5-Pentanediol as an Oxygen Precursor for Atomic Layer Deposition of Zinc Oxide Thin Films

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Experimental

ZnO thin films were deposited on p-type Si (100) substrates in a laminar flow type reactor (ATOMIC-CLASSIC, CN1 Co., Ltd.) by atomic layer deposition (ALD) by using diethylzinc (DEZ, 99.9999 %, Mecharonics Co., Ltd.) as a Zn precursor. As an oxygen precursor, deionized water and 1, 5-pentandiol (PD, $\geq$ 97.0 %, Sigma-Aldrich Co., Ltd.) were used for the typical ALD process and our new ALD process, respectively. Prior to the ALD process, the native oxide of the Si substrate was removed by using a dilute aqueous solution (1:100) of buffered oxide etcher (BOE). Bare Si substrates were immersed into the dilute BOE solution for 60 s and rinsed by deionized water for 15 s. Subsequently, water on the substrates was dried by blowing N_2. ALD sequence consisted of DEZ exposure-purge-oxygen precursor exposure-purge where each pulse time was controlled by solenoid valves. All the precursors were vaporized from external canisters at room temperature and led to the reactor through gas lines, which were maintained at 120 ^{o}C, without any carrier gas. The purging steps were performed with N_2 gas (400 sccm, 99.999 %), and the substrate temperature was calibrated with a thermocouple-implanted wafer under N2 atmosphere of 1 torr.

The film thicknesses were measured by spectroscopic ellipsometer (SE MG-1000, Nano-View Co., LTD.). Crystallinity was evaluated by XRD measurements (D/max-2500/PC, Rigaku). XPS analyses were performed on the PHI 5000 Versa Probe (ULVAC PHI, Japan) using a monochromatized Al Kα emission (1486.6 eV). Binding energies were measured using the C 1s peak (284.8 eV) of the adventitious carbon as an internal standard. Sputtering during the XPS depth profiling was performed with 2 keV Ar$^+$ ions. In order to observe the interfacial oxide, specimens for HR-TEM observation were prepared using focused ion beam (FIB, Quanta 3D, FEI), and the FE-TEM observation was performed on 300 keV (Tecnai F30UT, FEI).
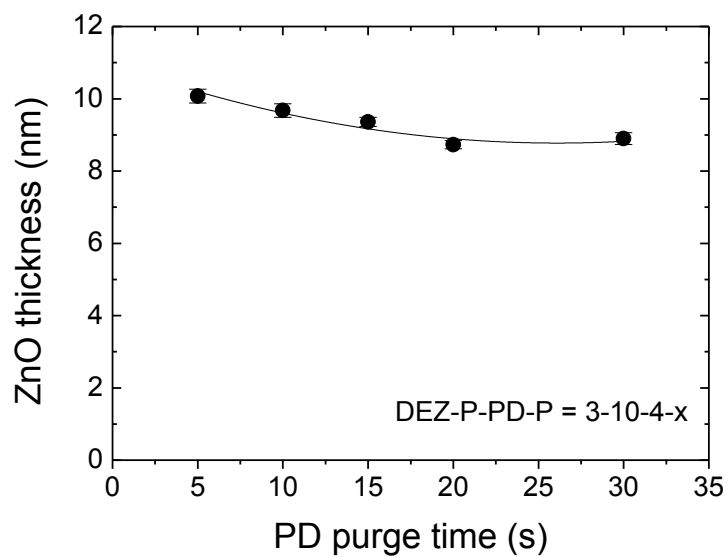
Figure S1. ZnO thickness as a function of a PD purging time. During the ALD process (80 °C), the exposure times of DEZ and PD were 3 and 4 s, respectively, and the purging time of DEZ was 10 s.
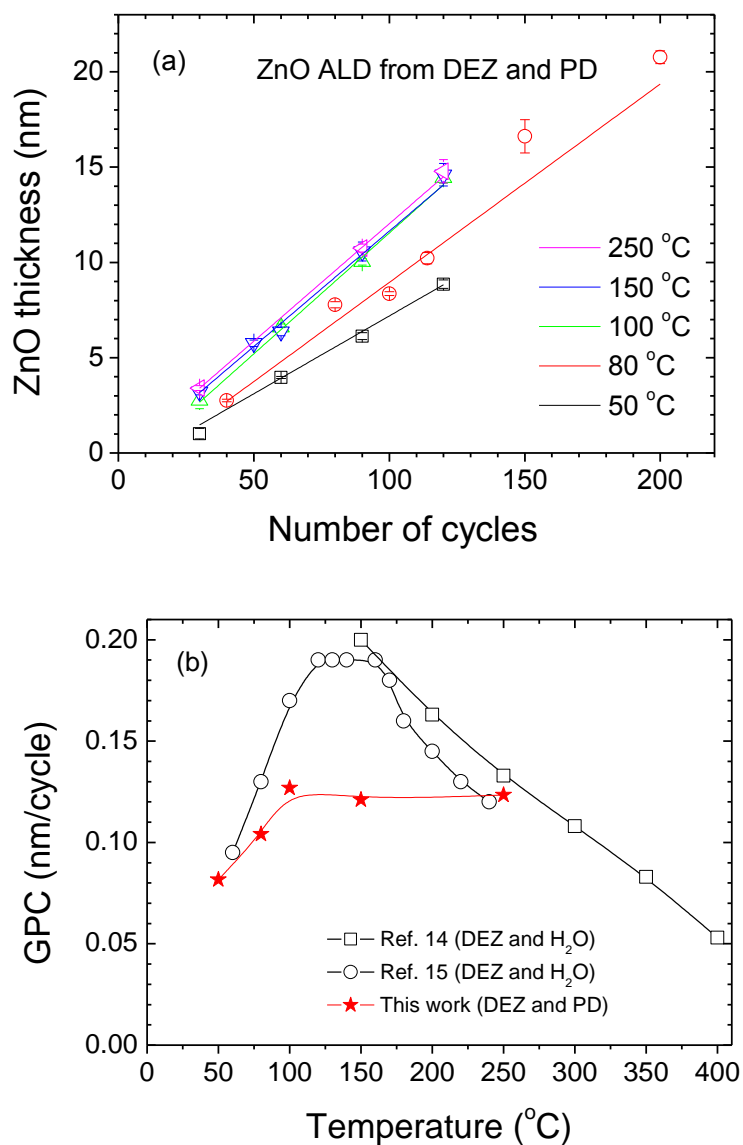
Figure S2. (a) plots of ZnO thickness versus number of ALD cycles at various temperatures. DEZ-Purge-PD-purge = 3-10-4-20 in sec. (b) comparison of GPC between the typical ZnO ALD using DEZ and water (Refs. 14 and 15) and the new ALD using DEZ and PD.
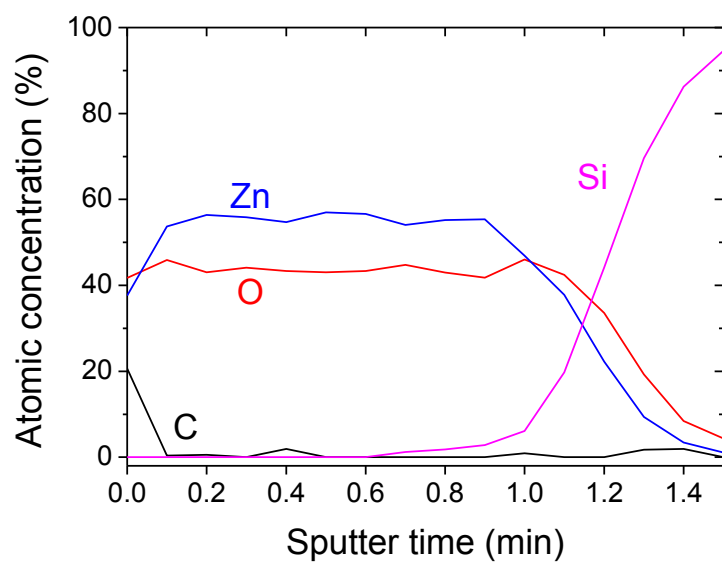
Figure S3. XPS depth profile of ZnO thin films grown at 80 ^{o}C by the typical ALD process from DEZ and water.
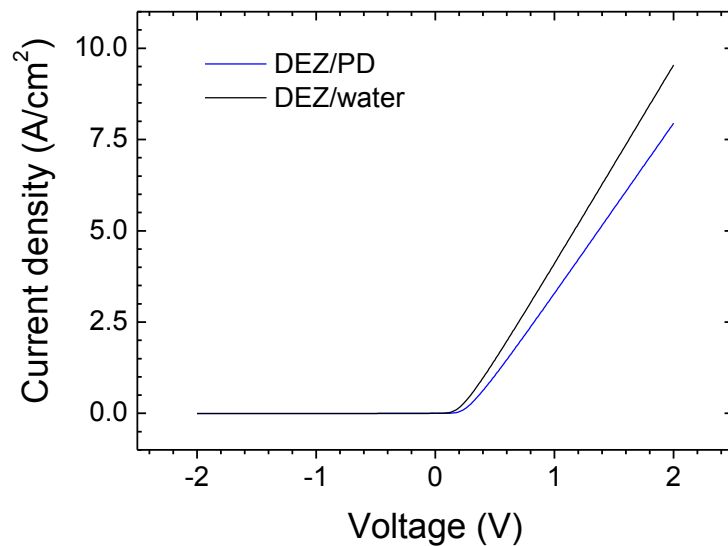
Figure S4. Current density-voltage curves of n-ZnO/p-Si diodes fabricated by DEZ/PD (blue) and DEZ/water (black) ALD processes.
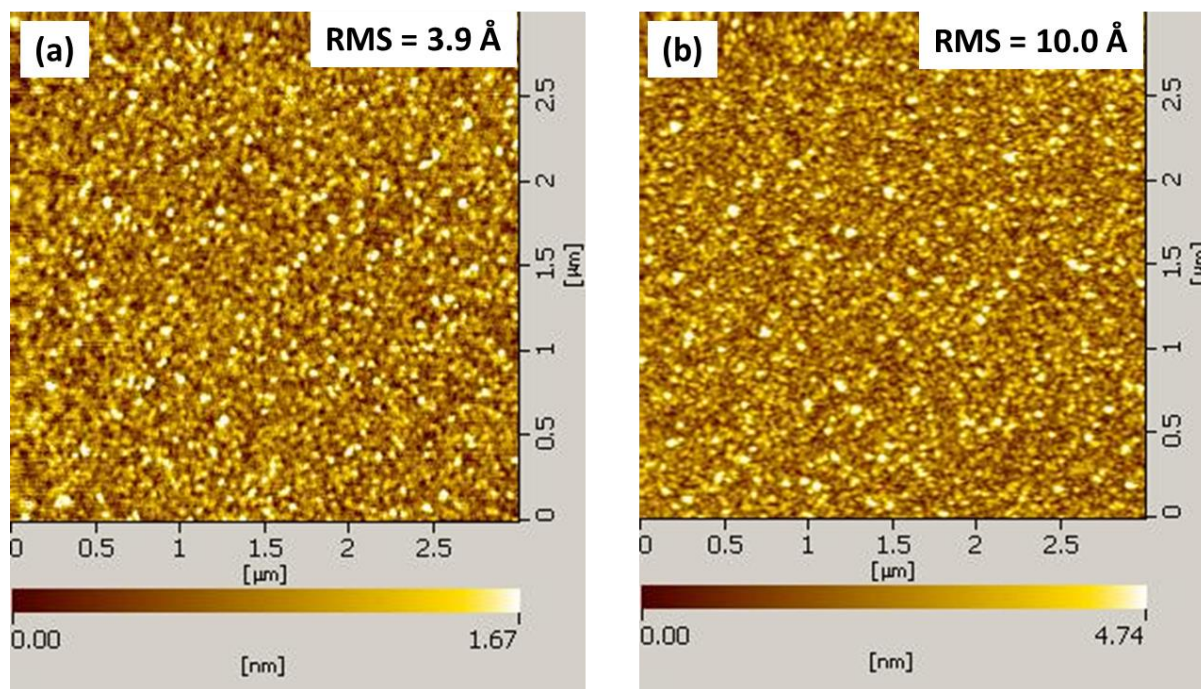
Figure S5. Atomic force microscopic images of ZnO films grown by DEZ/PD (a) and DEZ/water (b) processes at 80 °C, of which thicknesses are around 10 nm.
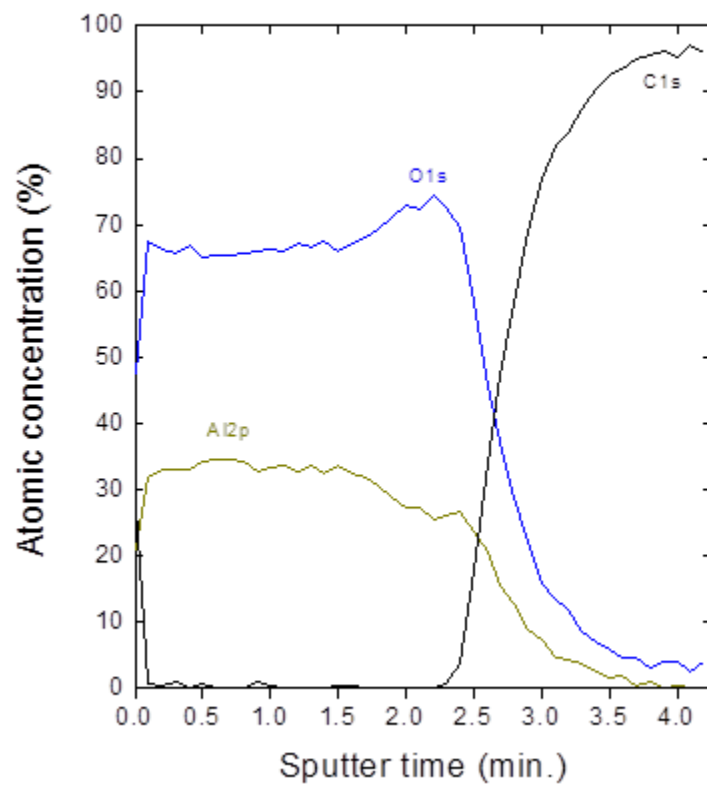
Figure S6. XPS depth profile of Al_2O_3 thin film grown at 80 °C on a polymer substrate by ALD using TMA and PD.
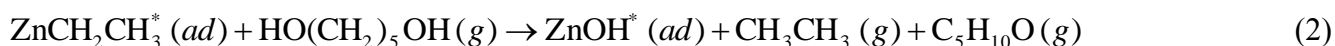
Supporting Information

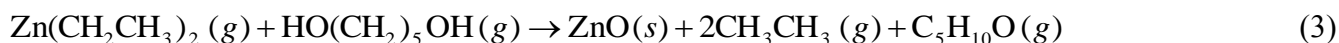Table S1. Standard enthalpies of formation and standard entropies (25 $^{\circ}$C)[a]

Substance	State	$\Delta H_f^{\,o}$ (kJ/mol)	$S^{\,o}$ (J/mol·K)
Al$_2$O$_3$	s	-1675.7	50.9
ZnO	s	-350.5	43.7
CH$_4$	g	-74.8	186.2
CH$_3$CH$_3$	g	-84.7	229.5
THP (C$_5$H$_{10}$O)	l	-254.8	-
	g	-223.8	-
Al(CH$_3$)$_3$	l	-149.7	209.4
	g	-86.5	-
Zn(CH$_2$CH$_3$)$_2$	l	18	290.2
	g	57	-
H$_2$O	l	-285.8	69.9
	g	-241.8	188.7
HO(CH$_2$)$_5$OH	l	-528.8	321.3
	g	-442.0	-

[a] The data were obtained from the thermodynamic data at http://webbook.nist.gov.

According to the proposed reaction pathway, the adsorption reactions during ZnO ALD from DEZ and PD can be described as

$$\text{ZnOH}^*\,(ad) + \text{Zn(CH}_2\text{CH}_3)_2\,(g) \rightarrow \text{ZnOZnCH}_2\text{CH}_3^*\,(ad) + \text{CH}_3\text{CH}_3\,(g) \tag{1}$$

$$\text{ZnCH}_2\text{CH}_3^*\,(ad) + \text{HO(CH}_2)_5\text{OH}\,(g) \rightarrow \text{ZnOH}^*\,(ad) + \text{CH}_3\text{CH}_3\,(g) + \text{C}_5\text{H}_{10}\text{O}\,(g) \tag{2}$$

where the asterisks denote the surface species. Therefore the overall reaction for ZnO ALD is

$$\text{Zn(CH}_2\text{CH}_3)_2\,(g) + \text{HO(CH}_2)_5\text{OH}\,(g) \rightarrow \text{ZnO}(s) + 2\text{CH}_3\text{CH}_3\,(g) + \text{C}_5\text{H}_{10}\text{O}\,(g) \tag{3}$$

By using the data listed in Table S1, the standard enthalpy of reaction ($\Delta_r H^{\,o}$) of the reaction 3 is calculated at 25 $^{\circ}$C as below:

$$\Delta_r H^{\,o} = \{-350.5 + 2\times(-84.7) + (-223.8)\} - \{57 + (-442.0)\} = -358.7\ \text{kJ/mol}$$

Similarly, the overall reaction for ZnO ALD from DEZ and H$_2$O can be described as

$$\text{Zn(CH}_2\text{CH}_3)_2\,(g) + \text{H}_2\text{O}\,(g) \rightarrow \text{ZnO}(s) + 2\text{CH}_3\text{CH}_3\,(g) \tag{4}$$

The $\Delta_r H^{\,o}$ of the reaction 4 at 25 $^{\circ}$C is:

$$\Delta_r H^{\,o} = \{-350.5 + 2\times(-84.7)\} - \{57 + (-241.8)\} = -335.1\ \text{kJ/mol}$$